

Carbonate Fuel Cell Technology and Materials

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Abstract

High-temperature carbonate fuel cells are recognized as the cleanest and most efficient power generation option for commercial and industrial customers. The first-generation carbonate fuel cell plants have shown an electrical efficiency of 45–48%. The electrolyte in this fuel cell is a mixture of alkali carbonates, and it operates at a high-enough temperature that the heat by-product can be used for cogeneration applications such as district heating, hot water, process steam, and absorption chilling for air conditioning. Alternatively, the heat by-product can be used with an unfired gas turbine for additional electrical generation. Depending on location, application, and load size, carbonate fuel cells are expected to achieve an overall energy efficiency of 65–80% in cogeneration and combined cycle applications. The cell hardware uses commonly available stainless steels. Electrode materials are nickel-based. Furthermore, standard, well-established manufacturing processes are employed. Therefore, carbonate fuel cells are well positioned to be cost-competitive with alternative technologies. Significant progress has been made in the development, manufacturing, product engineering, and field operation of carbonate fuel cell technology. Megawatt and submegawatt units are operating worldwide. A comprehensive review of carbonate fuel cell technology and materials are presented in this article.

Keywords: carbonate fuel cells, direct fuel cells, high-temperature fuel cells, internal reforming fuel cells.

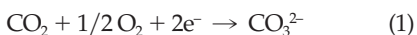
Carbonate Fuel Cells: Basic Concept

The fuel cell produces direct-current electricity from electrochemical reactions of a fuel and an oxidant. An electrolyte is deployed to support the reactions by transporting charged ions between the electrodes. The fuel cell is commonly named by the electrolyte it uses, which also determines the operating temperature, electrochemical reactions, and cell construction hardware of the fuel cell.

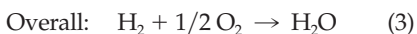
The carbonate fuel cell deploys a mixture of alkali carbonates as the electrolyte and operates at 550–650°C. The basic electrochemistry of carbonate fuel cells involves the formation of carbonate (CO_3^{2-}) at the cathode by the combination of oxygen, carbon dioxide, and two electrons; transport of the carbonate ions to the anode through carbonate electrolyte; and finally, reaction of the carbonate ion with

hydrogen at the anode, producing water, carbon dioxide, and two electrons:

Cathode reaction:



Anode reaction:



For each mole of hydrogen consumed in the anode compartment, one mole of carbon dioxide and one mole of water are produced. Hydrogen is made available to the anode in a carbonate fuel cell by extracting it from a common fuel (such as by steam-reforming natural gas). CO present

in the reformed fuel is also considered a fuel in this cell. Oxygen is supplied from air, and carbon dioxide is made available by recycling it from the anode exhaust. For this purpose, the anode exhaust is oxidized with the feed air in an oxidizer prior to its introduction into the cathode. Details on carbonate fuel cell chemistry are available in the *Fuel Cell Handbook*.¹

The fuel cell reactions use both H_2 and CO in the anode. The commonly available carbonaceous fuels need to be converted to a usable form, either inside or outside the cell. Steam reforming of a light hydrocarbon fuel in an external reformer is a well-established industrial process for hydrogen production for fuel cells. More than half of the carbonate fuel cell developers selected the external reforming approach for their carbonate fuel cell systems.²

The steam-reforming reaction is highly endothermic, and the fuel cell anode reaction is exothermic. While the product of the reforming reaction (hydrogen) is a reactant in the fuel cell anode, the fuel cell reaction product (water) is a reactant in the reforming reaction. The carbonate fuel cell system operates at high-enough temperatures to allow practical reforming reaction kinetics for the natural gas and other light hydrocarbons inside the fuel cell. Therefore, the thermal and chemical features of the fuel cell and reforming reactions are uniquely complementary for the efficient integration of both of these reactions inside the anode compartment of the carbonate fuel cell. FuelCell Energy Inc. (FCE) of Danbury, Conn., adopted this internal reforming approach for its Direct FuelCell (DFC) products.

DFCs incorporate features to carry out both the reforming and the fuel cell anode reactions inside the anode compartment and have the unique ability to generate electricity directly from a hydrocarbon such as natural gas without external conversion, as required with fuel cells employing external reforming. The DFC operating principle is illustrated in detail in Figure 1. A hydrocarbon fuel such as natural gas is introduced into the anode compartment along with steam. The overall fuel cell reaction is simply natural gas conversion with air to water and CO_2 . In the presence of the catalyst in the anode compartment, the fuel and water react to form hydrogen fuel. The heat required for the reaction is provided by the fuel cell. The hydrogen reacts electrochemically with CO_3^{2-} at the anode to release water, CO_2 , and heat, which is consumed in the reforming reaction; the remainder is removed from the fuel cell for isothermal operation. Two-thirds of the heat produced by

the fuel cell reaction is used up in the internal reforming reaction, resulting in a uniform fuel cell temperature.

The DFC concept eliminates the external reformer and associated heat-exchange equipment, resulting in a simple and efficient power plant. A simple system concept adopted by FCE for its products, as illustrated in Figure 2, incorporates single-pass airflow, single-pass fuel flow, and atmospheric pressure operation. The natural gas fuel, after sulfur clean-up, is preheated and humidified in a heat exchanger/vaporizer using the heat by-product carried off by the cathode exhaust. The fuel exhaust, containing water, CO₂, and spent fuel, is then oxidized in an anode exhaust oxidizer to preheat the incoming air and allow transfer of the CO₂ to the cathode inlet. The net heat by-product can be used for co-generation. Such a simple system uses the minimum amount of processing equipment among all fuel cell power plants.

Materials Technologies

This carbonate fuel cell operates at approximately 600–650°C. This is an optimal temperature that avoids the use of precious-metal electrodes required by lower-temperature fuel cells, such as PEM (polymer electrolyte membrane) and phosphoric acid fuel cells, and the more expensive metals and ceramic materials required by higher-temperature fuel cells, such as solid oxides. As a result, less expensive Ni-based electrocatalysts and readily available metals are used in carbonate fuel cell design.

A brief development history of carbonate fuel cell technology is shown in Figure 3. The carbonate fuel cell concept was first developed during the beginning of the last century. The basic cell design was established in the 1960s, while high-performance components were developed in the 1970s. Between 1980 and 2000, component and stack technologies were further improved, simplified, and verified in large-area stacks. Manufacturability and proof-of-concept power plants were demonstrated in >200 kW field testing. Since 2000, development has focused on field trials and commercialization. More than 40 units, ranging from 250 kW to 1 MW, have been successfully operated, the majority of them by FCE.

The construction of a carbonate fuel cell is illustrated in Figure 4. The bipolar plate and the corrugated current collectors are made of properly selected 300 series stainless steel. The electrodes are made from porous nickel-based materials. The matrix is ceramic lithium aluminate. The electrolyte is a mixture of lithium and potas-

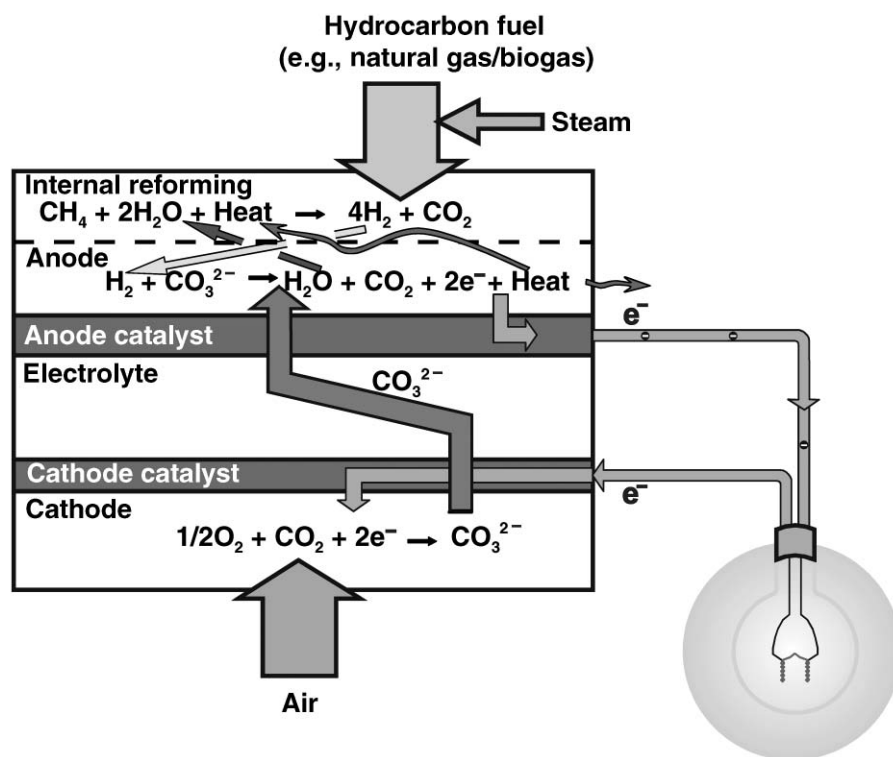


Figure 1. How the direct carbonate fuel cell works: synergistic and efficient heat and mass transfer results in high fuel cell efficiency.

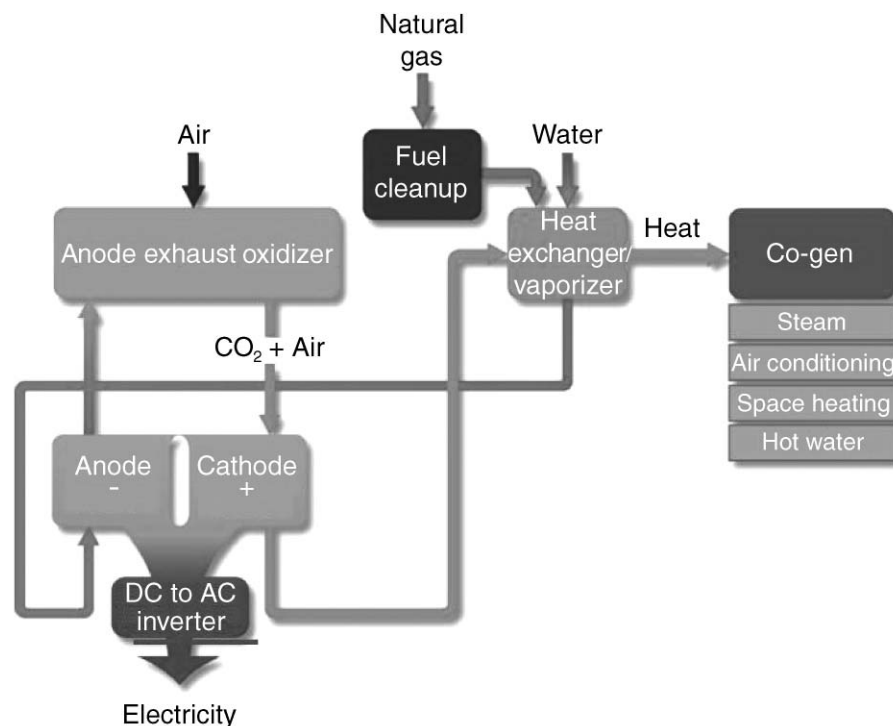


Figure 2. The simplicity of the Direct FuelCell system design allows minimal balance-of-plant equipment technology: an external reformer and associated heat-exchange equipment are not required.

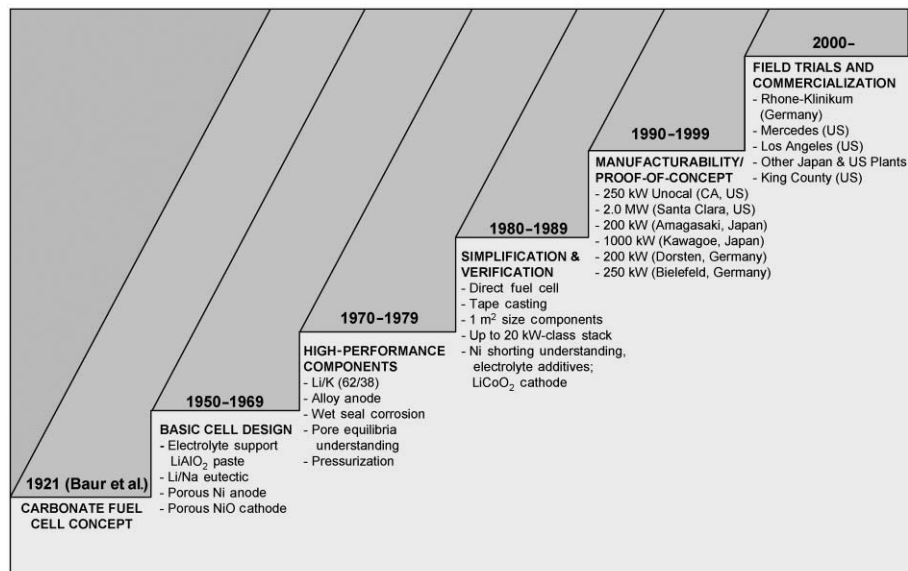


Figure 3. Development history of carbonate fuel cells: intensive global R&D during the past three decades has advanced the technology to a commercial level.

sium/sodium carbonate salts, which melt between 450°C and 510°C. The cell operates at 600–650°C, and the cell hardware components contact the electrolyte liquid. Material properties such as creep strength, sintering resistance, low compaction, hot corrosion resistance, and low carburization will affect cell life and durability. In addition, stable, long-term anode and cathode electrochemical activity is necessary.

The selection of carbonate fuel cell materials is based on intensive materials research carried out during the last three decades, focusing on characterizing the endurance of various components, optimizing the design for lowering costs, and confirming that the selected materials will provide at least five years (40,000 h) of useful/operational life. In the early years of development, hot corrosion of the

metallic hardware (for the bipolar separator plate and corrugated current collectors that provide the gas flow passages) in the carbonate environment was an important consideration. Endurance results^{5,4} have shown that properly selected 300 series stainless steel provides adequate corrosion protection for this application. Cost-effective corrosion protection of the wet seal surfaces has been a major focus of materials development efforts. Aluminization has been found to eliminate the observed wet seal surface corrosion. Low-cost aluminization approaches have also been identified.⁵

A search for mechanically stable anodes identified Ni-Cr and Ni-Al alloys as the preferred choices. A lithiated NiO cathode has been selected by most of developers.

Stability of the NiO cathode in the carbonate system has been achieved by controlling the basicity of the carbonate electrolyte. Alkali metal oxides are being used as electrolyte or cathode additives to manage the proper electrolyte acidity/basicity level.

The electrolyte matrix is a microporous ceramic structure made from $\gamma\text{-LiAlO}_2$ or $\alpha\text{-LiAlO}_2$ sandwiched between the electrodes of the fuel cell (Figure 5). The electrolyte is immobilized within the micropores of the matrix by a >0.3 MPa capillary force. Electrolyte distribution between the anode, cathode, and matrix is capillary-controlled. The pore sizes of the anode, cathode and matrix are designed to keep the matrix filled with electrolyte all the time while the anode and cathode remain partially filled, providing optimal performance. The electrolyte composition has historically been 62mol% Li_2CO_3 /38mol% K_2CO_3 . However, all the pressurized fuel cell stack developers have gradually switched over to Li/Na carbonate electrolyte, primarily to improve cathode stability, which is adversely affected by pressurized operation. Further details on the matrix and electrolyte can be found in component review articles.^{4,6} While baseline materials and components as described have been scaled up to ~1 m² for use in full-sized stacks, research continues in order to enhance performance and reduce costs. The search for alternative cathode materials and electrolytes is also being continued, primarily to extend the useful life of the fuel cell well beyond the five-year goal.

The size of commercial carbonate fuel cells is in the ~1 m² (10 ft²) range, a two order of magnitude increase in area from the size of early cells (3 cm²) developed during the past three decades. The full-height stack design of different systems varies with respect to gas manifolding and the number of cells in the stack. The major

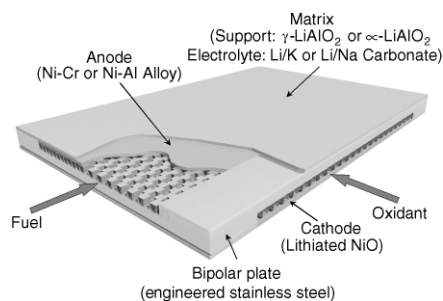


Figure 4. Package configuration for carbonate bipolar fuel cells: cell hardware employs stainless steel, and electrodes are nickel-based.

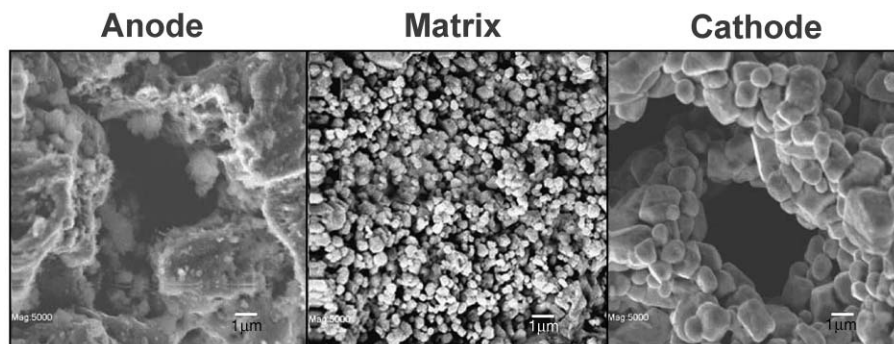


Figure 5. Morphology of carbonate fuel cell active components: the matrix (center image) with micropores is sandwiched between the fuel (anode, left image) and oxidant (cathode, right image) electrodes.

characteristics of carbonate fuel cells are (1) large cell area, largest among various fuel cell types; (2) small seal area and thus more efficient use of the active cell area; (3) ease of fabrication; and (4) lower cost. FCE and MTU CFC Solutions (Ottobrun, Germany) use ~350–400 cells in a full-height 250 kW stack. Figure 6 shows ~400 cells stacked in a bipolar configuration. Developers in Japan, meanwhile, have pursued a building-block approach. In this approach, a fewer number of cells, typically 80–120, are enclosed within the terminating plates, forming a building-block unit. Several of the building-block units are then stacked to build a truck-transportable full-height stack.

Product Manufacturing

Carbonate fuel cell construction employs commonly available stainless steels for the cell hardware, nickel-based electrode materials, and well-known manufacturing processes. Standard sheet metal forming, bending, and welding operations are involved in the manufacture of cell hardware components. The anodes and cathodes are manufactured by standard processing techniques such as tape casting. Matrix manufacturing by tape casting is also well developed. Most of the developers have demonstrated the ability to manufacture full-sized components. Five developers have already tested full-area cell stacks.

Carbonate Fuel Cell Product Status

Due to the simple system design and high efficiency of carbonate fuel cells, several developers around the world are

pursuing them for stationary power generation applications in the near term, and for large (10 MW or larger) power plants in the long term. Ishikawajima Harima Heavy Industries Co. of Japan is focusing on the development of coal-fueled large hybrid power plants based on its pressurized carbonate fuel cell. The fuel in this case is derived from a coal gasifier, which provides a clean way to utilize coal. In the near term, the company has launched field-testing of 300 kW natural gas units. The first prototype unit was tested in 2003 at Kawagoe, Japan. Additional tests on coal gas and biogas units have also been planned. A team from the Korean Institute of Science and Technology and the Korean Electric Power Research Institute is in an early stage of development of large multi-megawatt systems using coal gas. This team is testing a 100 kW system and has plans to test a 250 kW system in the near term.

An Italian-Spanish team led by Ansaldo Fuel Cells is focusing on large systems based on its pressurized fuel cell technology. In the near term, the researchers are focusing on a 500 kW system. MTU CFC Solutions has developed a 250 kW stationary fuel cell plant (called a hot module) for combined heat and power (CHP) applications and has already placed ten hot-module units at customer sites. The company's plants operating in Bad Berka, Munich, and Cartagena are being used for CHP and air conditioning (a three-way generator scheme commonly referred to as "trigen"). The company has reported 47% electrical and >80% overall thermal efficiencies for its cogeneration system.

FCE is currently commercializing carbonate fuel cell products for commercial and industrial customers and is continuing to develop the next generation of large-sized carbonate fuel cell products for increased power density and longer life. FCE's current products, the DFC300A, DFC1500, and DFC3000, are rated in capacity at 250 kW, 1 MW, and 2 MW, respectively, and are scalable for distributed applications up to 10 MW or larger. These products are designed to meet the base load power requirements of a wide range of commercial and industrial customers, including wastewater treatment plants (such as municipal sewage treatment facilities and industrial food processors and breweries), telecommunications/data centers, manufacturing facilities, office buildings, hospitals, universities, prisons, mail processing facilities, hotels and government facilities, and in grid support applications for utility customers. Through February 2005, over 62 million kWh of electricity has been generated from power

plants incorporating DFC technology at customer sites throughout the world. Other carbonate fuel cell companies have not produced a substantial amount of electricity, nor published data on their electricity production.

Product Attributes and Market Drivers

It is expected that distributed resources will make up a growing proportion of new and replacement generation capacity in developed as well as emerging markets. Because of its modularity and high-efficiency operation, carbonate fuel cell technology seems suited to commercial or industrial cogeneration applications or utility distributed generation. The main disadvantage is the high initial cost of the system.

FCE's carbonate power plants currently have achieved electrical efficiencies of 45–48% and have the potential to reach an electrical efficiency of 57% at product maturity in single-cycle applications. In addition, power plants can achieve an overall energy efficiency of 70–80% for combined heat and power applications.

Carbonate power plants have significantly lower emissions of greenhouse gases and particulate matter than conventional combustion-based power plants. They emit virtually no NO_x or SO_x and have been designated "ultraclean" by the California Air Resources Board (CARB).⁷ The comparative emissions of fuel cell power plants versus traditional combustion-based power plants, as compiled by the U.S. Department of Energy/National Energy Technology Laboratory and company product specification sheets, are listed in Table I.

Carbonate power plants can use many fuel sources, such as natural gas, industrial and municipal wastewater treatment gas, propane, and coal gas (escaping gas from active and abandoned coal mines as well as synthesis gas processed from coal).

The technology is in its early state of commercial use and the production volume is low. As such, the product cost is currently high for potential applications. In the near term, government-sponsored incentive programs are facilitating product sales. In the longer term, product cost reductions through power density increases, lower material costs, and higher production volumes will lessen or eliminate the need for incentives.

Methane-rich gas produced by the anaerobic digestion of organic wastes (biogas) offers a unique opportunity for carbonate fuel cells. Industrial wastewater and municipal treatment facilities that produce biogas represent a promising



Figure 6. Full-sized fuel cell stack: ~400 stacked cells terminated by end plates.

Table I: Emissions of Fuel Cell Power Plants versus Traditional Combustion-Based Power Plants.

	NO _x Emissions (lbs/MWh)	SO ₂ Emissions (lbs/MWh)
Average U.S. Fossil Fuel Plant	4.200	9.210
Microturbine (60 kW)	0.490	0.000
Small Gas Turbine (250 kW)	0.467	0.000
Combined-Cycle Gas Turbine	0.230	0.005
Carbonate Fuel Cell, Single-Cycle (Direct FuelCell)	0.016	0.000

Source: FuelCell Energy Inc., Form 10-K, p. 11, January 14, 2005.

market. The methane produced from the anaerobic digester process is the fuel to generate the electricity that powers the wastewater treatment plant. The fuel cell heat can be used to heat the sludge to facilitate anaerobic digestion. Moreover, wastewater treatment gas is a renewable fuel eligible for incentive funding for project installations throughout the world.

Outlook

While various fuel cell systems are emerging as new options for power generation, carbonate fuel cell plants are suitable for generating high-efficiency

electricity or combined heat and power for stationary applications. Over 40 units ranging from 250 kW to 1 MW are in field operation worldwide. These units have shown 45–47% electrical conversion efficiencies (on a lower heating value basis) and overall thermal efficiencies approaching 80% in combined heat and power applications. The plant emissions are ultraclean. These attributes and the various incentives available for high-efficiency ultraclean renewable fuel technologies are helping market entry of carbonate fuel cells in stationary applications. As the technology matures and costs are lowered

by materials improvement, the products are expected to capture broader commercial acceptance, paving the way for larger multi-megawatt systems.

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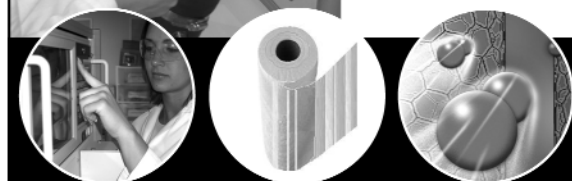
Water Sorption Isotherms up to 85°C.



Quantachrome Instruments' Hydrosorb-HT water sorption analyzer features an analysis temperature range of 12 to 85°C. Such capability makes this, the latest advance in water sorption technology, of particular interest to those working with PEM fuel cells. Both the HT and standard model (12 to 47°C range) are equipped with a two-speed stirred thermostatted bath for improved temperature stability, and an indicating thermal sensor for improved operator feedback.

The Hydrosorb™ series of water sorption analyzers brings a historically slow analysis (days, even weeks) up to speed (overnight, maybe just a few hours) by its combination of intelligent operating algorithms and accurate vapor pressure measurement. Its rugged design has also done away with the need for microbalances and so the Hydrosorb is equally at home in industrial labs as it is in academia.

Quantachrome also manufactures H₂ sorption, surface area, pore size and density analyzers, and offers analytical services.



From left to right: Hydrosorb features fingertip operation, polymer electrolyte membrane (PEM), gas sorption in nano carbons.

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